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High resolution NMR spectra of polyacrylonitrile and its two-unit and three-unit model compounds

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HIGH RESOLUTION NMR SPECTRA OF POLYACRYLONITRILE AND ITS TWO-UNIT AND THREE-UNIT MODEL COMPOUNDS

BY MASAO MURANO

The NMR spectra of PAN and PAN- ad_1 were measured in NaCNS-D₂O solution and nitromethane-ethylenecarbonate solution.

The different spectrum was obtained in both solutions and this may be derived from the difference of the chemical shifts between the geminal protons of isotactic (*meso*) methylene (ν_{KL}). But this behavior cannot be found in the model compounds. In determining the tacticity of PAN, the line width of two methylene resonance and the value of ν_{KL} are important factors.

The relation between the NMR spectra of PAN and the model compounds is also discussed.

Introduction

The tactic structure of polyacrylonitrile (PAN) has been studied by many investigators with various methods, but it is not yet determined definitely. The high resolution NMR spectroscopy is a useful method for determining the tactic structure, so the tacticities of many high polymers have been evaluated by this method. We measured the NMR spectra of PAN and PAN- ad_1 in NaCNS-D₂O solution, and it was found that the tacticity in terms of diads can be determined from the methylenic proton resonance of PAN¹⁾. From the analysis of the NMR spectra of the two-unit model compounds, 2,4-dicyanopentane (2,4-DCNP), it was shown that the *racemic* (syndiotactic) methylene protons appear at higher field than those of *meso* (isotactic) methylene²⁾. The tacticities of PAN and PAN- ad_1 prepared under various polymerization conditions were determined and it was also reported that almost all PAN are rich in syndiotactic form and do not show any stereospecificity³⁾. The tacticity is calculated, assuming that the *meso* methylenic protons are equivalent because the methylenic proton resonance of PAN- ad_1 shows only two peaks and the methylenic proton resonance of PAN can be analyzed as the superposition of two kinds of triplets¹⁾³⁾.

On the other hand, Matsuzaki *et al.*⁴⁾ measured the NMR spectrum of PAN in DMF- d_7 solution and reported that PAN has a completely random configuration because PAN- ad_1 shows two peaks with equal intensity.

Bargon *et al.*⁵⁾ reported from the NMR spectrum of PAN in nitromethane-ethylenecarbonate

(Received August 15, 1969)

- 1) R. Yamadera and M. Murano, *J. Polymer Sci.*, **B3**, 821 (1965)
- 2) M. Murano and R. Yamadera, *J. Polymer Sci.*, A-1, **5**, 1072 (1967)
- 3) R. Yamadera and M. Murano, *J. Polymer Sci.*, A-1, **5**, 1059 (1967)
- 4) K. Matsuzaki, T. Uryu, M. Okada, H. Shiroki, *J. Polymer Sci.*, A-1, **6**, 1475 (1968)
- 5) J. Bargon, K.H. Hellwege and U. Johnsen, *Kolloid-Z.*, **213**, 51 (1966)

solution, that PAN is rich in isotactic form. In these three solutions, the isotactic methylenic protons of PAN are thought to be equivalent.

Recently, Yoshino *et al.*⁶⁾ measured the NMR spectrum of PAN- α , β - d_2 in perchloric acid at 100 Mc/sec and reported the non-equivalence of isotactic methylene. As mentioned above, many different theories have been presented about the interpretation for the NMR spectrum of PAN but they are not interpreted comprehensively compared with each other, because the solvents and the samples used in these reports are different from each other.

In this report, the difference in the NMR spectra of PAN measured in various solutions using the same sample are discussed in a comprehensive interpretation about the NMR spectrum of PAN. In addition, the NMR spectra of the two-unit model (2,4-DCNP)²⁾ and the three-unit model compounds, 2,4,6-tricyanoheptane (2,4,6-TCNH)⁷⁾, are also analyzed to be compared with those of PAN.

Experimental

Polymerization

Acrylonitrile (AN) and α -deuteroacrylonitrile (AN- ad_1) were polymerized in benzene solution at 60°C with azobisisobutyronitrile as an initiator. PAN was also obtained with γ -irradiation on AN-urea canal complex at -78°C.

Preparation of model compounds

The preparation of 2,4-DCNP and 2,4,6-TCNH and the separation into stereoisomers were reported in the previous papers²⁾⁷⁾.

NMR spectrum

The NMR spectra of PAN and PAN- ad_1 were measured at various temperatures in 50% D_2O solution of NaCNS (NaCNS- D_2O) and in nitromethane-ethylenecarbonate (1 : 1) mixed solvent.

Varian A-60 and HR-60 spectrometers were used, operating at 60 Mc/sec. The NMR spectra of the model compounds were measured at various temperatures in NaCNS- D_2O , and nitromethane-ethylenecarbonate. The double resonance spectra with the side band method were also measured.

Results and Discussion

NMR spectra of PAN and PAN- ad_1

The NMR spectra of PAN in NaCNS- D_2O solution and in nitromethane-ethylenecarbonate solution were compared in Fig. 1. The multiplet at higher field is assigned to the methylenic protons and the multiplet at lower field to the methine protons.

The methylenic proton resonance shows mainly six peaks in both solvents and can be thought to be superposition of two kinds of triplets. But the relative intensity of them is different in each

6) T. Yoshino, H. Kenjo and N. Hisano, *J. Polymer Sci.*, B5, 703 (1967)

7) M. Murano and R. Yamadera, *J. Polymer Sci.*, A-1, 6, 843 (1968)

High Resolution NMR Spectra of Polyacrylonitrile

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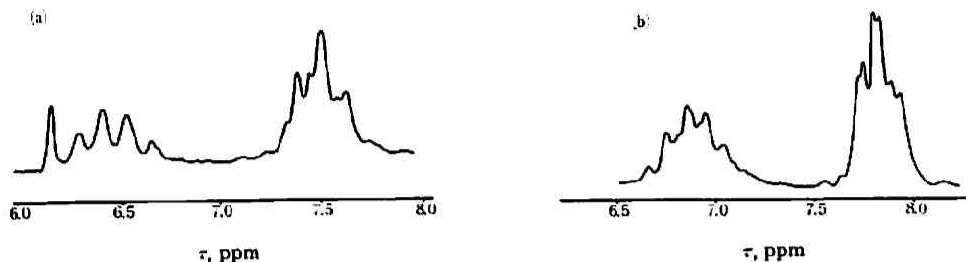


Fig. 1 NMR spectra of PAN at 60 Mc/sec
(a) in NaCNS-D₂O at 120°C (b) in CD₃NO₂-(CH₂O)₂CO at 150°C

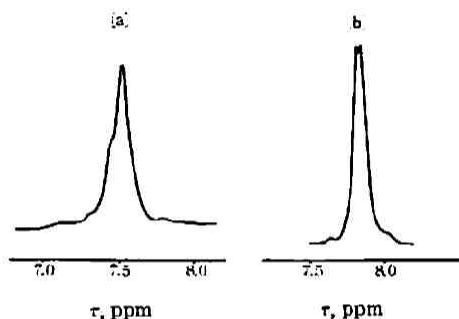


Fig. 2 Methylenic proton resonance of PAN-*d*_{α1} at 60 Mc/sec
(a) in NaCNS-D₂O at 120°C
(b) in CD₃NO₂-(CH₂O)₂CO at 150°C

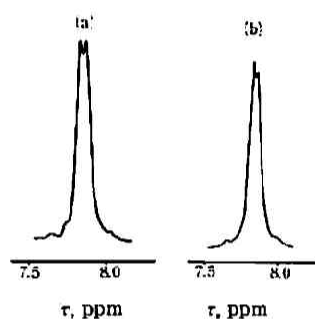


Fig. 3 Methylenic proton resonance of PAN-*αd*₁ at 60 Mc/sec in CD₃NO₂-(CH₂O)₂CO
(a) at 150°C (b) at 100°C

solvent, so the tacticity in terms of diads cannot be determined by only comparing the height of their peaks. This fact can be seen more definitely in the NMR spectra of PAN-*αd*₁ shown in Fig. 2. In NaCNS-D₂O solution, methylenic proton signal consists of two singlets with different intensity, while in nitromethane-ethylenecarbonate, two peaks are observed with almost equal intensity. Furthermore, in the case of nitromethane-ethylenecarbonate solution, the relative intensity of these two peaks depends upon temperature. The peak at higher field rapidly decreases its intensity as temperature decreases (Fig. 3), although this phenomenon was not found in NaCNS-D₂O solution.

NMR spectra of model compounds

The NMR spectra of model compounds of PAN have been already reported^{2,7)}. In this report, another part of them is discussed. Fig. 4 shows the NMR spectra of the *racemic* form and *meso* form of 2,4-DCNP in NaCNS-D₂O solution and Fig. 5 those in nitromethane-ethylenecarbonate. In Table 1 the coupling constants and chemical shifts obtained from the analysis of these spectra are summarized. In Fig. 6 the NMR spectra of heterotactic 2,4,6-TCNH are shown, and the results obtained from the analysis of 2,4,6-TCNH are shown in Tables 2 and 3. Comparing the two kinds of

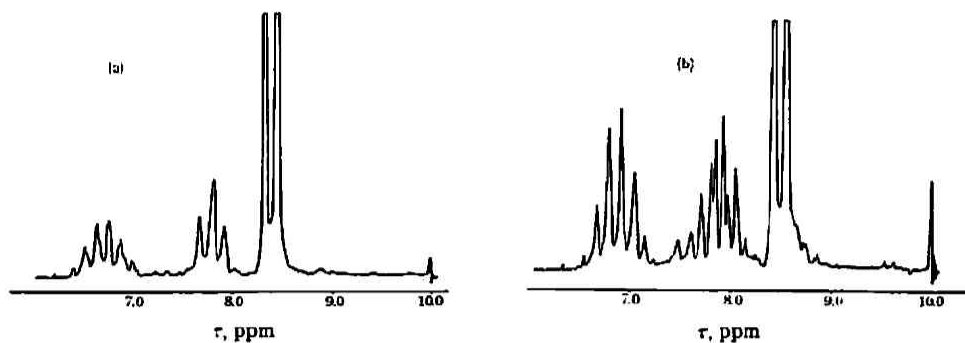


Fig. 4 NMR spectra (a) *racemic* 2,4-DCNP (b) *meso* 2,4-DCNP at 60 Mc/sec in NaCNS-D₂O at 25°C

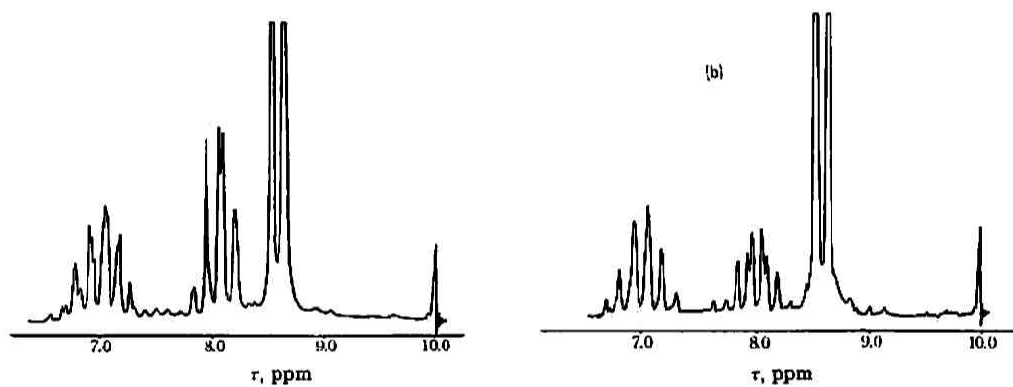


Fig. 5 NMR spectra (a) *racemic* 2,4-DCNP (b) *meso* 2,4-DCNP at 60 Mc/sec in CD₃NO₂-(CH₂O)₂CO at 25°C

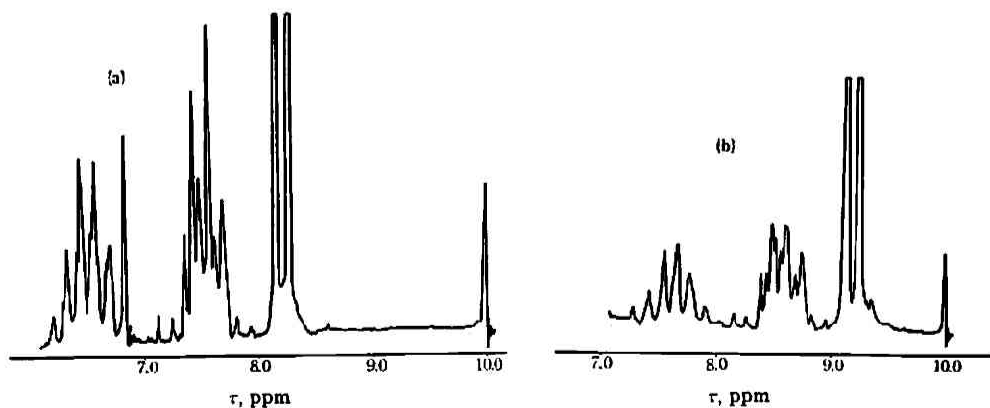


Fig. 6 NMR spectra of heterotactic 2,4,6-TCNH at 60 Mc/sec (a) in NaCNS-D₂O (b) in CD₃NO₂-(CH₂O)₂CO at 25°C

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Table 1 Chemical shifts and coupling constants of 2,4-DCNP
(NaCNS-D₂O)

Isomers	Chemical shifts (ppm)				Coupling constants (cps)					
	CH ₃	CH ₂	ν^*_{KL}	CH	CH ₃ -CH J_{AX}	CH ₂ J_{KL}	CH ₂ -CH			
							J_{AK}	J_{BL}	J_{AL}	J_{BK}
<i>meso</i>	8.40	7.77 $\left(\begin{smallmatrix} 7.66 \\ 7.38 \end{smallmatrix} \right)$	0.22	6.74	7.5	13.5	7.5	7.5	7.5	7.5
<i>racemic</i>	8.40	7.82	0	6.72	7.5	13.5	7.5	7.5	7.0	7.0

(CD₃NO₂-(CH₂O)₂CO)

Isomers	Chemical shifts (ppm)				Coupling constants (cps)					
	CH ₃	CH ₂	ν_{KL}	CH	CH ₃ -CH J_{AX}	CH ₂ J_{KL}	CH ₂ -CH			
							J_{AK}	J_{BL}	J_{AL}	J_{BK}
<i>meso</i>	8.61	8.04 $\left(\begin{smallmatrix} 7.93 \\ 8.16 \end{smallmatrix} \right)$	0.23	7.00	7.3	14.2	7.5	7.5	7.5	7.5
<i>racemic</i>	8.61	8.11 $\left(\begin{smallmatrix} 8.07 \\ 8.14 \end{smallmatrix} \right)$	0.07	6.98	7.3	14.2	6.9	8.1	8.1	6.9

* The difference in chemical shifts between two protons in methylene resonance

Table 2 Chemical shifts and coupling constants of heterotactic 2,4,6-TCNH
(NaCNS-D₂O)

	Chemical shifts (ppm)					Coupling constants (cps)					
Isomers	CH ₃	CH ₂	ν _{KL}	CH		CH ₃ -CH J _{ΔX}	CH ₂ J _{KL}	CH ₂ -CH			
				2,6	4			J _{ΔK}	J _{BL}	J _{AL}	J _{BK}
<i>meso</i> part	8.26	7.51 ^{(7.42} _{7.61}	0.19	6.50	6.52	7.5	13.5	7.5	7.5	7.5	7.5
<i>racemic</i> part		7.55	0	6.51		7.5	13.5	7.5	7.5	7.0	7.0

(CD₃NO₂-(CH₂O)₂CO)

	Chemical shifts (ppm)					Coupling constants (cps)					
Isomers	CH ₃	CH ₂	ν _{KL}	CH		CH ₃ -CH J _{AX}	CH ₂ J _{KL}	CH ₂ -CH			
				2,6	4			J _{AK}	J _{BL}	J _{AL}	J _{BK}
<i>meso</i> part	8.51	7.87 ^(7.78) _(7.97)	0.19	6.90	6.92	7.3	14.2	7.5	7.5	7.5	7.5
<i>racemic</i> part		7.95 ^(7.92) _(7.99)	0.07			7.3	14.2	6.9	8.1	8.1	9.9

Table 3 Chemical shifts and coupling constants of 2,4,6-TCNH (NaCNS-D₂O)

Isomers		Chemical shifts (ppm)				Coupling constants (cps)					
		CH ₃	CH ₂	CH		CH ₃ -CH <i>J</i> _{AX}	CH ₂ <i>J</i> _{KL}	CH ₂ -CH			
				2,6	4			<i>J</i> _{AK}	<i>J</i> _{BL}	<i>J</i> _{AL}	<i>J</i> _{BK}
syndio		8.26	7.55	6.47	6.46	7.5	13.5	7.5	7.5	7.0	7.0
hetero	<i>meso</i>	8.26	7.51 ^(7.42) 7.61	6.50	6.52	7.5	13.5	7.5	7.5	7.5	7.5
	<i>racemic</i>		7.55	6.51		7.5	13.5	7.5	7.5	7.0	7.0
iso		8.26	7.52 ^(7.47) 7.58	6.53	6.57	7.5	13.5	7.5	7.5	7.5	7.5

methylene in 2,4-DCNP, the *racemic* form appears higher than *meso* form (Table 1) in both solvents. The heterotactic-2,4,6-TCNH shows the same (Table 2). From this fact, the two kinds of methylene in PAN can be assigned as follows: the higher field peak to *racemic* methylene and the lower to *meso* one. In *meso* 2,4-DCNP, no remarkable difference can be found between both solvents, while the *racemic* one shows different behavior in both solvents. In NaCNS-D₂O, *racemic* 2,4-DCNP shows a spectrum which means the complete equivalence of methylenic protons ($\nu_{KL}=0$), and it does not depend on temperature. But in nitromethane-ethylenecarbonate solution, it shows a nonequivalent spectrum ($\nu_{KL}\neq 0$) and this tendency is clearer at low temperature. At high temperature it becomes equivalent (Fig. 7). The same tendency is found in DMF solution. This fact may mean that the conformation of the *racemic* form is fixed to some extent in these solvents at low temperature.

This phenomenon can be found in the *racemic* part of heterotactic 2,4,6-TCNH.

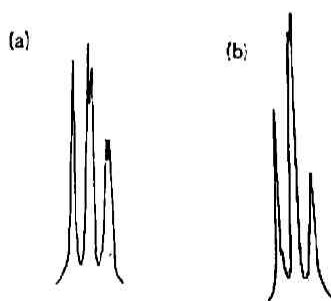


Fig. 7 Methylenic proton resonance of *racemic* 2,4-DCNP at 60 Mc/sec in CD₃NO₂-(CH₂O)₂CO
(a) at 25°C
(b) at 120°C

The chemical shifts of hydrogen attached to 4th position in 2,4,6-TCNH, which can be thought to represent the configuration of triads in PAN, are shown in Table 3. The methine protons show the isotactic-CH, heterotactic-CH and syndiotactic-CH resonance, respectively, from the higher field. The difference in chemical shifts between geminal protons of isotactic methylene (ν_{KL}) takes smaller value in isotactic 2,4,6-TCNH than in *meso* 2,4-DCNP. This fact may be important to analyze

the NMR spectrum of PAN. This tendency is found between the two-unit and three-unit model compounds of polyvinylchloride⁹⁾.

NMR line width

As shown in Fig. 2, the NMR spectrum of PAN- αd_1 in nitromethane-ethylenecarbonate has two peaks and the line width of the *racemic* methylene resonance at higher field is larger than that of the *meso* methylene resonance at lower field. This difference in line width becomes more definite at low temperature. The same difference between two kinds of methylene has been found in polyvinylchloride⁹⁾ and polymethylmethacrylate¹⁰⁾, and it has been reported that there is a difference in the mobility of solution between the isotactic segment and the syndiotactic segment and the peak of the syndiotactic part shows broader than that of the isotactic part. This phenomenon is not so remarkable in NaCNS-D₂O solution. As mentioned above, the model compound shows the same behavior: the methylenic protons of *racemic* 2,4-DCNP and the *racemic* part in 2,4,6-TCNH show the non-equivalent resonance in nitromethane-ethylenecarbonate solution, while they show the equivalent resonance in NaCNS-D₂O solution. From these facts, the difference in line width between the isotactic methylene and the syndiotactic one may be attributed to the conformation of PAN in solution.

Tacticity of PAN

The tacticity in terms of diads is determined from the ratio of the area of the *meso* methylene resonance and the *racemic* methylene resonance. The line width is an important factor in comparing the area. Changing the value of the line width, the spectrum of PAN- αd_1 was constructed by superposing the syndiotactic methylene upon the isotactic one in order to get a good agreement with the observed spectrum. As shown in Fig. 8, the tacticity is greatly changed by slight change in line width. Fig. 8(b) shows the best agreement with the observed spectrum. The same superposition was tried for PAN and in Fig. 9(b) the best agreement was obtained.

In the previous reports,^{11,12)} the tacticity was determined assuming that the isotactic methylene is equivalent in NaCNS-D₂O solution. In this report, the tacticity is obtained with the assumption

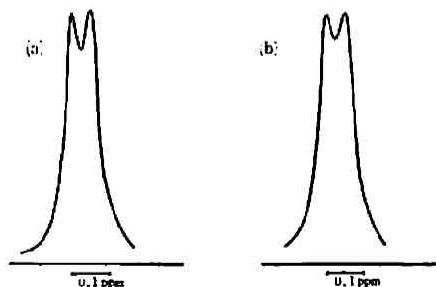


Fig. 8 The superposition of two peaks with equal height changing the line width to get a good agreement with the observed spectrum of PAN- αd_1 in CD₃NO₂-(CH₂O)₂CO at 150°C.

(a) $b=0.02:0.03$ ppm, $s=30:70$

(b) $b=0.025:0.03$ ppm, $s=40:60$

$2b$: half height width

s : ratio of the area of isotactic methylene to that of syndiotactic one

8) Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh and R. Chujo, *J. Polymer Sci.*, A-1, 4, 1413 (1966)

9) S. Satoh, T. Kuroda, S. Enomoto and M. Asahina, *Rep. Prog. Polym. Phys. Japan*, 9, 63 (1966)

10) Y. Kato and A. Nishioka, *J. Polymer Sci.*, B3, 739 (1965)

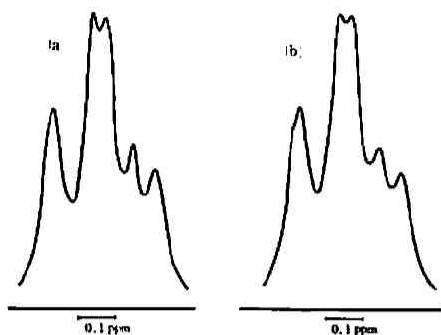


Fig. 9 The superposition of two kinds of triplet with equal height changing the line width to get a good agreement with the observed methylene resonance of PAN in $\text{CD}_3\text{NO}_2\text{-(CH}_2\text{O)}_2\text{CO}$ at 150°C .

(a) $b=0.02:0.03\text{ppm}$, $s=30:70$

(b) $b=0.025:0.03\text{ppm}$, $s=40:60$

$2b$: half height width

s : ratio of the area of isotactic methylene to that of syndiotactic one.

that the isotactic methylene is non-equivalent. The observed spectrum shows six peaks in the methylene resonance. This spectrum can be obtained by superposing the six main peaks of isotactic methylene upon the triplet of syndiotactic methylene as well as by superposing two kinds of triplet. (Fig. 10) The methylene resonance of PAN- αd_1 is a superposition of a quartet upon a singlet if the isotactic methylene is non-equivalent. In this case, one of the main two peaks of isotactic methylene has almost the same chemical shifts as that of syndiotactic methylene, so the spectrum mainly consists of two peaks. (Fig. 11)

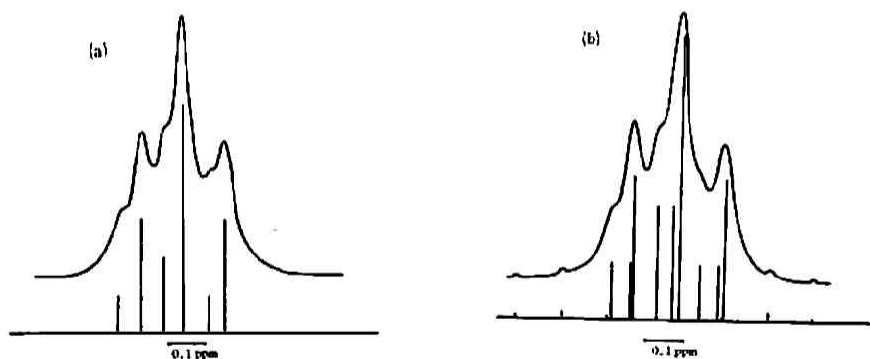


Fig. 10 The superposition of two kinds of methylene assuming (a) the equivalence of isotactic methylene ($b=0.025\text{ ppm}$, $s=25:75$) and (b) non-equivalence of isotactic methylene ($b=0.025\text{ ppm}$, $s=45:55$) to get a good agreement with the observed methylene resonance of PAN in $\text{NaCNS-D}_2\text{O}$

The difference between the two spectra assuming equivalence and non-equivalence of isotactic methylene is small peaks appeared both side of the main peaks. In the observed spectra of PAN and PAN- αd_1 in $\text{NaCNS-D}_2\text{O}$ solution, four and two small peaks can be found, and these peaks become larger in 100 Mc/sec (Fig. 12). ν_{KL} of isotactic methylene can be calculated from these small peaks to be $\nu_{\text{KL}}=9$ at 60 Mc/sec and 15 cps at 100 Mc/sec. This value is almost the same as that obtained from *meso* 2,4-DCNP, but pretty larger than that of isotactic 2,4,6-TCNH. But the detection of these peaks is very difficult and there may remain some problem in determining whether these small

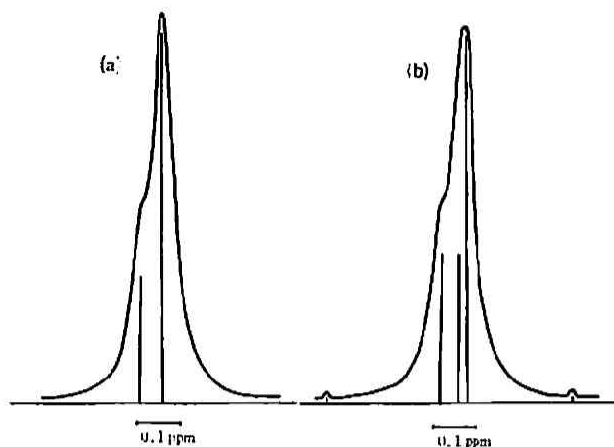


Fig. 11 The superposition of two kinds of methylene assuming (a) the equivalence of isotactic methylene ($b=0.025$ ppm, $s=25:75$) and (b) non-equivalence of isotactic methylene ($b=0.025$ ppm, $s=45:55$) to get a good agreement with the observed methylene resonance of PAN- αd_1 in NaCNS- D_2O

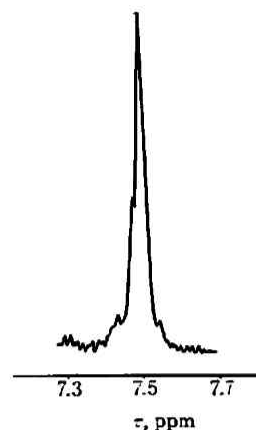


Fig. 12 NMR spectrum of PAN- αd_1 at 100 Mc/sec in NaCNS- D_2O at 120°C

peaks are assigned to the isotactic methylene or to the impurities such as heterolinkages.

Although the small peaks are also found on both sides of the main peaks in nitromethane-ethylenecarbonate solution (Figs. 1(b) and 2(b)), if one takes the assumption that the isotactic methylene is equivalent in this solution and non-equivalent in NaCNS- D_2O solution, the resultant tacticity is in good agreement in both solutions. But this assumption cannot be confirmed from the analysis of the model compounds. (Table 1)

As shown in Fig. 13, the methine proton resonance decoupled from the methylenic protons consists of three peaks and these peaks may represent the configuration in terms of triads. From the

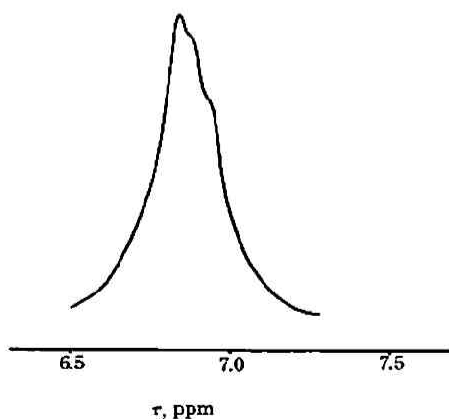


Fig. 13 The methine proton resonance of PAN at 60 Mc/sec decoupled from the methylenic protons in $CD_3NO_2-(CH_2O)_2CO$ at 150°C

results of 2,4,6-TCNH (Table 3), these three peaks may be assigned to syndiotactic-CH, heterotactic-CH and isotactic-CH from the lower field. This spectrum shows that PAN is syndiotactic rich polymer.

Polyvinylchloride is one of the polymers studied by the NMR technique to determine the tacticity, and there have been reported many opinions about the spectrum of the isotactic methylene. The methylene resonance decoupled from the methine protons¹¹⁾ and the analysis of the three-unit model compounds⁹⁾ show that the isotactic methylene is to be equivalent, but recently the 100 Mc/sec spectrum has been shown to be non-equivalent by Johnsen *et al.*¹²⁾ who first reported that the isotactic methylene is equivalent. Thus, there remains some problem about this point. In the case of PAN, some detailed studies will be necessary to solve this problem.

NMR spectra of PAN obtained from other conditions

The study of the NMR spectra of PAN which may have different tacticity will give us a new information about the analysis of the NMR spectra. For this object, PAN is obtained with γ -irradiation on AN-urea canal complexes. Fig. 14 shows the NMR spectra of this polymer.

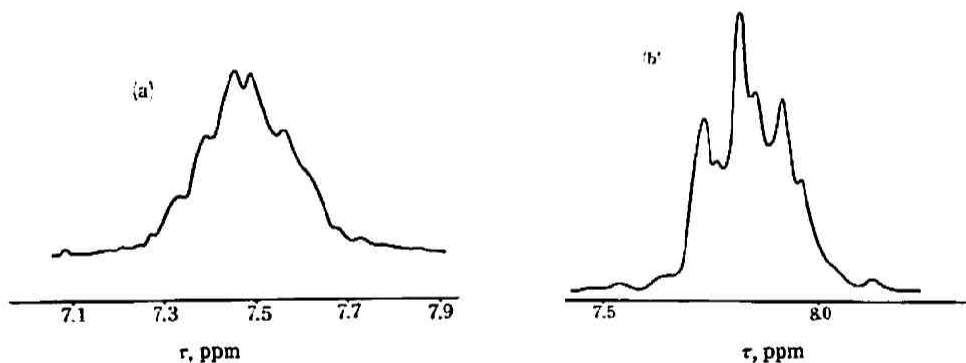


Fig. 14 The methylenic proton resonance of PAN at 60 Mc/sec prepared with γ -irradiation on urea-AN canal complexes (a) in NaCNS- D_2O at 120°C (b) $CD_3NO_2-(CH_2O)_2CO$ at 150°C

In NaCNS- D_2O solution (Fig. 14(a)), the spectrum consists of two kinds of triplets with equal intensity. Assuming the equivalence of isotactic methylene, one can get 50/50 for the value of the ratio syndio/iso⁹⁾. While taking the non-equivalence of isotactic methylene, the two kinds of triplets are assigned to the isotactic methylene, and so this polymer is almost isotactic, which is in good agreement with the result reported by Yoshino *et al.*⁶⁾

In nitromethane-ethylenecarbonate solution (Fig. 14(b)), the different spectrum was obtained. If one assumes that the isotactic methylene is equivalent in this solution, this spectrum shows that this PAN is isotactic rich.

11) F. A. Bovey, E. W. Anderson, D. C. Douglass and J. M. Mason, *J. Chem. Phys.*, **39**, 1199 (1963); S. Satoh, *J. Polymer Sci., A*, **2**, 5221 (1964)

12) J. Bargon, K. H. Hellwege and U. Johnsen, *Makromol. Chem.*, **95**, 187 (1966)

If this polymer is isotactic rich, some different behaviors from the ordinary PAN may be expected in the infrared spectrum, x-ray diffraction pattern and density. And these studies may be important to determine the tactic structure of PAN.

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